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Polyphosphazenes are a broad, novel class of inorganic-organic macromolecules. The physical properties of polyphosphazenes can be understood in terms of a highly flexible backbone, with various physical or chemical characteristics tailored by the incorporation of specific side groups. As part of our program to synthesize new materials with hybrid macromolecular properties, the synthesis and characterization of several IPNs containing phosphazene polymers is described.

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SYNTHESIS AND CHARACTERIZATION OF POLY(ORGANOPHOSPHAZENE) INTERPENETRATING POLYMER NETWORKS

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SYNTHESIS AND CHARACTERIZATION OF POLY(ORGANOPHOSPHAZENE) INTERPENETRATING POLYMER NETWORKS

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Abstract:

Polyphosphazenes are a broad, novel class of inorganic-organic macromolecules with the general formula $[NPR_2]_n$. The physical properties of polyphosphazenes can be understood in terms of a highly flexible backbone, with various physical or chemical characteristics tailored by the incorporation of specific side groups. As part of this program to synthesize new materials with hybrid macromolecular properties, the synthesis and characterization of several IPNs containing the phosphazene polymers poly[bis(2-(2-methoxyethoxy)ethoxy) phosphazene] and poly[bis(propyl oxybenzoate)phosphazene] with several organic polymers including polystyrene, poly(methyl methacrylate), polyacrylonitrile and poly(acrylic acid) is reported.

Introduction.

Most interpenetrating polymer networks (IPNs) are prepared using organic polymers. With the exception of polysiloxanes (1-8), little work has been published describing the syntheses of IPNs from inorganic-organic polymers. Inorganic-organic polymers generally have a high thermo-oxidative stability coupled with unusual combinations of properties that depend on the side groups attached to the backbone. Some common examples of inorganic-organic polymers include polysilanes, polysiloxanes and polyphosphazenes, depicted in Scheme 1(9). The synthesis and characterization of some of the first interpenetrating polymer networks (IPN) containing poly(organophosphazenes) with organic polymers are described in this paper (10-11).

Scheme 1 near here.

Poly(organophosphazenes) are a unique class of inorganic-organic polymers with alternating phosphorous and nitrogen atoms in the backbone and two organic, inorganic or organometallic side groups attached to each phosphorous (12-16). Their physical properties and applications can be tailored by the choice of the organic side group attached to the backbone. Due to this unique ability to tune their properties and applications by the choice of side groups, polyphosphazenes are an excellent choice for the preparation of IPNs . Table 1 lists some advantages of the polyphosphazene system.

Table 1 near here.

Polyphosphazenes are usually non-burning materials and may be highly flame retardant. This is due to the fact that phosphorous in its highest valency state can interfere with the

combustion pathway. A combination of phosphorous and nitrogen often yields compounds with enhanced flame retardant properties. Secondly, some polyphosphazenes possess a high degree of solvent-and-oil resistance. This makes them valuable materials for many industrial applications such as O-rings, gaskets and fuel lines. Another advantage of the polyphosphazene system is that many of these materials have a high degree of biocompatability. This property depends on the side group structure, with fluoroalkoxyphosphazenes being of particular interest. Some polyphosphazenes possess high flexibility and low glass transition temperatures (T_g). This characteristic makes many phosphazene polymers useful as low temperature elastomers and flexible thermoplastics. Probably the biggest advantage of the polyphosphazene system is the ease with which the polymeric molecular structure may be tuned to afford different properties and applications. This molecular tuning is accomplished by the linkage of different side groups to the polymer backbone (12-16). IPNs with combinations of poly(organophosphazenes) and other polymers would combine the advantages of polyphosphazenes with those of the other systems.

Poly(organophosphazenes) are prepared by the route summarized in Scheme 2. Commercially available hexachlorocyclotriphosphazene (1) undergoes a thermal ring opening polymerization at 250 °C to form poly(dichlorophosphazene) (2), a long-chain polymer with 15,000 or more repeating units. Poly(dichlorophosphazene) is hydrolytically sensitive, but the system may be stabilized against hydrolysis through halogen replacement reactions using a wide variety of nucleophiles, including sodium alkoxides and aryloxides or primary and secondary amines. These substitution reactions have yielded a large number of stable poly(organophosphazene) derivatives, the properties and applications of which depend on the side group structure (17-19).

Scheme 2 near here

Chart 1 shows examples of phosphazene polymers with different side groups. The first, poly[bis(p-oxybenzoic acid) phosphazene] (3) is water soluble as its sodium salt, and can be ionically cross-linked using calcium or other di or higher valent cation salts (20-22). The second example, poly[bis((3-amino propyl)pentamethyldisiloxane)phosphazene] (4) contains silicon atoms within the side groups and possesses elastomeric properties (23). Poly[bis(2-(2-methoxy ethoxy) ethoxy)phosphazene] (5) is water soluble. It is also an excellent solid solvent for salts such as lithium trifluoromethanesulfonate, and is being developed as a solid electrolyte material (24-28). Finally, when transannular ferrocenyl groups are attached to the polymer backbone, as seen in polymer 6, the system is electroactive and may be used as an electrode mediator material (29).

Chart 1 near here.

Some common applications for poly(organophosphazenes) include O-rings which are flexible at low temperature and have a high solvent-and-oil resistance; oil seal gaskets; fuel lines; shock absorber components with a high level of vibrational energy absorption; and finally carburetor and fuel injector components. As mentioned previously, polyphosphazenes are an excellent choice for these types of applications because of their non-burning characteristics, high flame retardancy, high levels of both solvent-and-oil resistance, and high degree of materials flexibility.

Specific derivatives are also being developed for uses in the field of biomedicine. Figure 1 shows an example of a polyphosphazene/organic polymer IPN which is available commercially as a shock-absorbing denture liner. Poly(organophosphazenes) are employed for dental and oral surgical applications because of their high degree of fungal resistance (30-33).

Figure 1 near here.

Syntheses of Poly(organophosphazenes).

The phosphazene polymers used in this IPN study were synthesized as described in Scheme 3. Polymer 5 was prepared by allowing poly(dichlorophosphazene) (2) to react with the sodium salt of 2-(2-methoxyethoxy)ethanol. The product polymer is poly[bis(2-(2-methoxy ethoxy)ethoxy)phosphazene] (MEEP) (5). MEEP is an unusual, hydrophilic phosphazene polymer, which is soluble in both water and organic solvents and has a T_g of -84 °C (24-25). Polymer 7 was prepared by allowing poly(dichlorophosphazene) (2) to react with the sodium salt of propyl p-hydroxybenzoate. This synthesis yields poly[bis(propyl p-oxy benzoate)phosphazene] (POBP) (7) a hydrophobic, elastomeric polymer with at T_g of -23 °C. This polymer is soluble in many organic solvents (21).

Scheme 3 near here.

Both the POBP (7) and MEEP (5) undergo crosslinking when exposed to ^{60}Co γ-radiation (24-25). Scheme 4 shows a mechanism proposed for the cross-linking of MEEP during exposure to ^{60}Co γ-radiation (34). Radiation probably generates radicals on any of the five carbon atoms in the MEEP side chains. Trans-combination of these radicals would form cross-links. Solid, uncross-linked MEEP has little resistance to viscous flow. However, after cross-linking, MEEP has an increased structural integrity and swells, without dissolving, in water or organic solvents. Figure 2 shows a sample of MEEP after cross-linking and after the swelling of a cross-linked portion in water for several hours. Cross-linked MEEP is capable of swelling to over ten times its original volume.

Scheme 4 near here.

Figure 2 near here.

Synthesis of IPNs.

In normal sequential IPN preparation, a monomer is first polymerized and crosslinked using either thermal or radiation techniques, to form a cross-linked polymer matrix (35-36). This cross-linked matrix is then allowed to imbibe a second monomer, a polymerization initiator, and a cross-linker to form a monomer-swollen, cross-linked polymer matrix. The second monomer is then polymerized and cross-linked within the matrix of the first to form the IPN. This general procedure for the preparation of a sequential IPN is shown in Scheme 5.

Scheme 5 near here.

In all the IPN syntheses described here, a preformed phosphazene polymer, either MEEP (5) or POBP (7), was used as the initial cross-linked polymer system. The organic polymers prepared within the polyphosphazene matrix include polystyrene (PS) (8), poly(methyl methacrylate) (PMMA) (9), polyacrylonitrile (PAN) (10), and poly(acrylic acid) (PAA) (11). The structures of the component materials are depicted in Chart 2.

Chart 2 near here.

These organic polymers were chosen because they represent a cross section of common macromolecules. In addition, their ease of polymerization, using thermal methods, for PS and PMMA, and by exposure to ^{60}Co γ-radiation, for PAN and PAA, made them an attractive choice.

Scheme 6 near here.

Polyphosphazene/organic polymer IPNs were prepared as summarized in Scheme 6. The polymerized polyphosphazene was exposed to ^{60}Co γ-radiation to form a cross-linked polymer matrix (34). The cross-linked matrix was then allowed to swell in a mixture of the organic monomer, azobisisobutyronitrile (AIBN) initiator, and ethylene glycol dimethacrylate cross-linker, until the swollen matrix had increased approximately ten times in volume. The imbibed organic monomer was then polymerized and cross-linked within the polyphosphazene matrix using either thermal techniques (PS and PMMA) or by exposure to additional ^{60}Co γ-radiation (PAN and PAA).

The objective was to incorporate the maximum amount of organic polymer into the cross-linked poly(organophosphazene) matrix. The ratio of components within the IPN system was estimated using ^{1}H NMR spectroscopy, and the values are depicted in Table 2. The ratios ranged from a 1:1 ratio of polyphosphazene polymer to organic polymer in the MEEP /PS IPN to a 4.5:1 ratio of polyphosphazene to organic polymer in the IPN containing POBP /PAN.

Table 2 near here.

Once prepared, the IPNs were purified and then characterized using conventional methods, including ^{1}H and ^{31}P NMR spectroscopy, FT-IR spectroscopy, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) (35-36). ^{1}H and ^{31}P NMR spectroscopy and FT-IR spectroscopy . FT-IR and NMR analyses are useful mainly to confirm the presence of both macromolecular constituents in the IPN systems, and to monitor the polymerization of the organic monomer by following the loss of vinyl protons.

Characterization.

DSC is an excellent technique for examining the miscibility of the components within an IPN system and for probing the intermolecular interactions that may exist between the component polymers. This may be accomplished by comparing the T_g values of the IPN system with those of its component macromolecules. The displacement of the values of the IPN T_g's from those of the component materials gives a general indication of both the degree of miscibility within the sample, and of interactions which may take place between the component materials (35-36). The IPN T_g values and those for the component materials are listed in Table 3.

Table 3 near here.

For example, an IPN containing MEEP and polystyrene with glass transition temperatures at -70 and +57 °C, can be compared to the T_g's of the parent component materials which occur at -84 °C (MEEP) and +100 °C (PS). This displacement of 15 and 40 °C shows that a good degree of miscibility exists within the system and that strong intermolecular interactions probably exist between the component materials.

In a second example, an IPN containing MEEP and PMMA has T_g's at -80 and +112 °C. These values may be compared to those of the component materials for which transition temperatures are at -84 °C (MEEP) and +105 °C (poly(methyl methacrylate)). Because the IPN T_g's are displaced 5 °C from those of the component materials, it appears that only a low degree of inter-component interactions exist within this system.

Finally, a single glass transition temperature seen in a DSC thermogram indicates a high degree of miscibility within the IPN system and a high degree of intermolecular interactions between the component macromolecules. Two of the polyphosphazene/organic polymer IPNs studied contain a single T_g. MEEP/PAN and POBP/PAA showed single T_g's at +34 and +54 °C, respectively. These materials apparently enjoy a high degree of miscibility and presumably a high degree of intermolecular interaction.

Scheme 7 near here.

Scheme 7 shows a representation of intermolecular interactions that might exist between a phosphazene polymer and an organic polymer within an IPN system. These interactions include hydrogen bonding, dipole-dipole interactions, and van der Waals forces. The interactions are shown in more detail in Scheme 8.

Scheme 8 near here.

For example, a MEEP side group could undergo hydrogen bonding with the side unit of PAA through the etheric oxygen of the MEEP and the acidic proton of the acrylic acid side group. MEEP could also undergo dipole-dipole interactions with PAN as depicted in Scheme 8. Finally, any poly(organophosphazene) could, in principle, undergo van der Waals interactions with any organic polymer. A good example is POBP and PS .

Each poly(organophosphazene) and organic polymer combination is capable of undergoing one or more type of these different intermolecular interactions, as listed in Table 4. MEEP is a hydrogen bond acceptor and is capable of undergoing dipole-dipole interactions. POBP is also a hydrogen bond acceptor and possesses hydrophobic qualities. Polystyrene is a

hydrophobic material and may undergo van der Waals interactions while PMMA is a hydrogen bond acceptor and undergoes dipole-dipole interactions. PAN undergoes dipole-dipole interactions while PAA is a hydrogen bond donor and also experiences dipole-dipole interactions. It is important to realize that these intermolecular interactions could increase the miscibility of the IPN components by binding the component polymers into a coherent material. However, even when favorable intermolecular interactions are built into the system, it may be impossible to predict the final miscibility of the IPN and whether or not these interactions will influence that miscibility (37-40).

Table 4 near here.

The following are specific descriptions of typical polyphosphazene/organic polymer IPNs. In the first example, an IPN containing MEEP and PAN is an amber, transparent, hard material that swells only slightly in water. This limited swelling behavior could be due to intermolecular interactions such as dipole-dipole interactions between the component materials or to the degree of cross-linking within the system. Its DSC thermogram, shown in Figure 3 contains a single, broad glass transition at +34 °C. This indicates that a high degree of miscibility exists within the system and there are favorable intermolecular interactions between the component polymers. The high degree of miscibility is reflected in the TEM micrograph shown in Figure 4. It shows a widely dispersed, almost web-like structure of the lightly colored organic polymer throughout the darker phosphazene matrix. It is interesting that, due to the relatively high electron density of the polyphosphazene phosphorous-nitrogen backbone, no staining of the sample was required when preparing TEM micrographs of poly(organophosphazenes).

Figure 3 here.

Figure 4 here.

A second example, is an IPN containing POBP and PS. This system forms a tough, opaque, white, elastomeric material which swells in organic solvents. Its DSC thermogram, depicted in Figure 5, shows two T_g's at +14 and +90 °C. These values are each displaced from those of the component materials by approximately 10 °C. Therefore this system appears to be less miscible than the previous example. The lower degree of miscibility is also reflected in its TEM micrograph shown in Figure 6. Here definite domains of the lightly colored organic polymer are evident dispersed throughout the darker colored polyphosphazene system.

Figure 5 here.

Figure 6 here.

Another example, is an IPN composed of MEEP and PMMA. This IPN is a tough, opaque, white, elastomeric material which swells to a high degree in organic solvents. Its DSC thermogram also shows two T_g's which occur at -80 and +112 °C. Both values are displaced only 5 °C from the component materials whose T_g values occur at -84 °C (MEEP) and +105 °C (PMMA). This small displacement indicates a very low degree of miscibility within the system and probably reflects the poor intermolecular interactions between the component materials. The low miscibility of the system is also evident from the TEM micrograph shown in Figure 7. Large domains of both the poly(organophosphazene) and the organic polymer throughout the IPN system are clearly evident.

Figure 7 here.

A fourth example, is an IPN composed of POBP and PMMA. This material is opaque with a slight golden hue. It is also elastomeric and swells in organic solvents. Its DSC thermogram shows two T_g's at +14 and +50 °C. These values are displaced approximately 15 and 50 °C from those of their component polymers which occur at -23 °C (POBP) and +105 °C (PMMA). The larger degree of displacement indicates that this system is more miscible than the previous one. The increased miscibility is also obvious from the TEM micrograph, shown in Figure 8, where a definite domain structure is evident of the lightly colored organic polymer throughout the polyphosphazene matrix.

Figure 8 near here.

The final example is an IPN containing POBP and PAA, a transparent, hard material which swells only slightly in organic solvents. The limited swelling behavior could reflect hydrogen bonding between the POBP and the acrylic acid side groups. This system shows a single T_g at +54 °C in its DSC thermogram which indicates a high degree of miscibility and good intermolecular interactions within the material. This behavior is also reflected in the TEM micrograph (Figure 9) which shows a domain structure of the lightly colored organic polymer bordered by an almost web-like structure of the phosphazene polymer.

Figure 9 near here.

Conclusion.

The synthesis and characterization of novel interpenetrating polymer networks composed of poly(organophosphazenes) and a selected series of organic polymers has been accomplished. Additionally, DSC and TEM methods were used to investigate miscibility and phase structure in the new materials. When the miscibility is low, these IPNs show properties

similar to those of their component polymers but exhibit hybrid properties when the components are highly miscible. Intermolecular interactions such as hydrogen bonding, dipole-dipole interactions or van der Waals forces between the macromolecular components could enhance miscibility within an IPN system. These phosphazene containing IPNs are the first members of new classes of multi-component polymeric materials which may possess unique technological and biomedical properties.

Future work in the area of polyphosphazene/organic or inorganic polymer IPNs includes the preparation of ion specific poly(organophosphazene)/organic polymer IPNs which may be used as ionic filters or ion exchange media. These types of materials could be used for both environmental and biomedical applications. The synthesis and characterization of IPNs composed of poly(organophosphazenes) and polysiloxanes is also being investigated.

Acknowledgement: This work was supported by the Office of Naval Research and the National Institute of Health.

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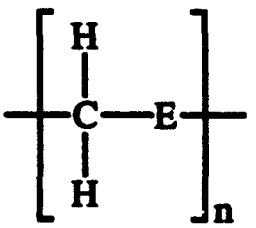
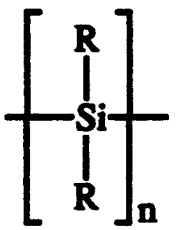
Scheme 1.

Organic Polymers

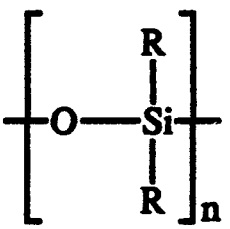


E = $C(R)_2$, O, or S

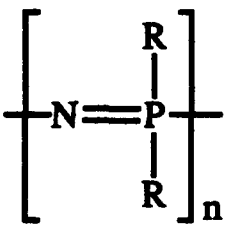
Inorganic Polymers



Polysilane



Polysiloxane

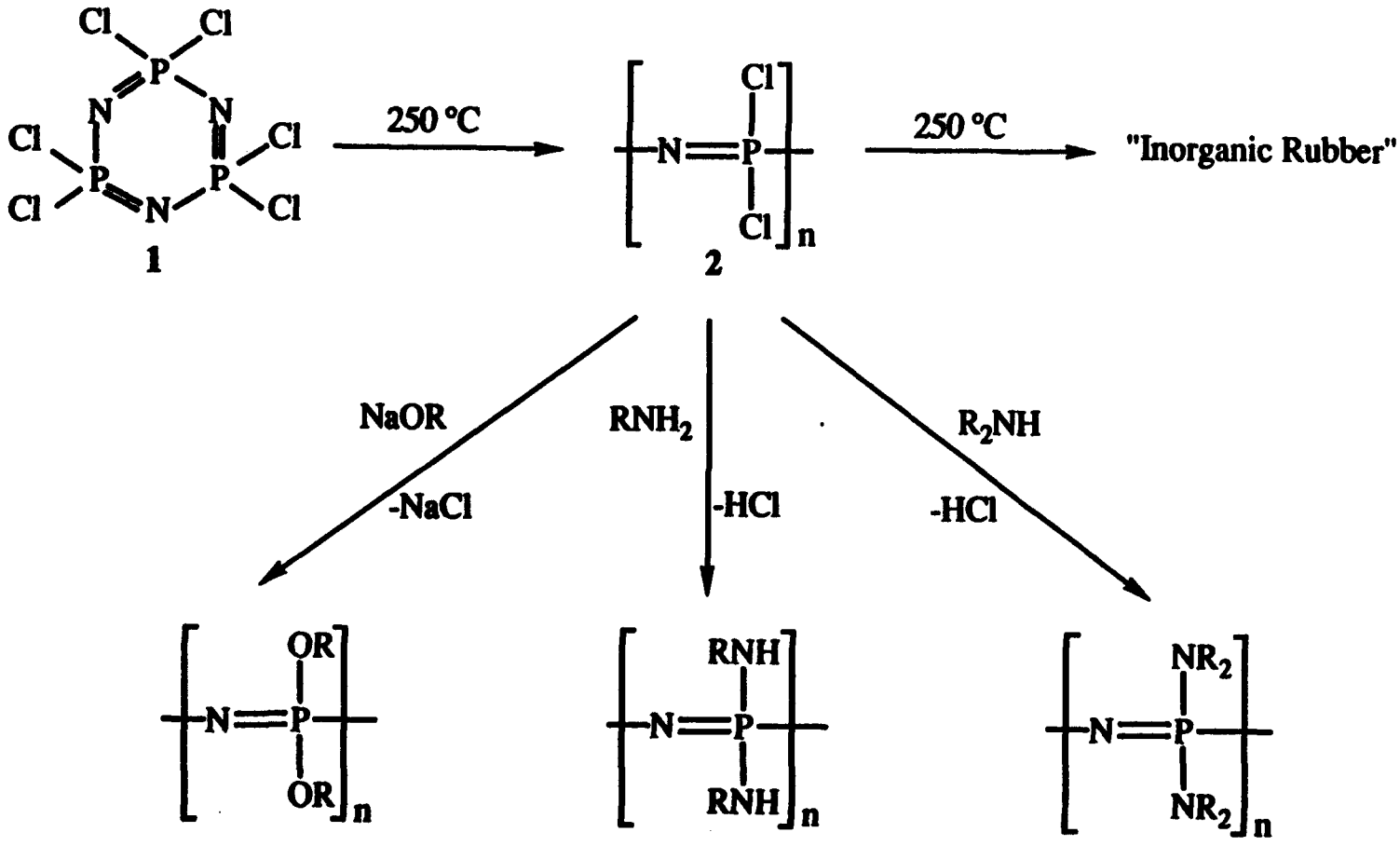


Polyphosphazene

Table 1.

Advantages of Polyphosphazenes as IPN Components
* Non-Burning and Flame Retardant
* Solvent and Oil Resistance
* Biomedical Compatibility
* Materials Flexibility (Low Tg)
* Ease of Tuning Molecular Structure

Scheme 2. General Synthesis of Poly(organophosphazenes



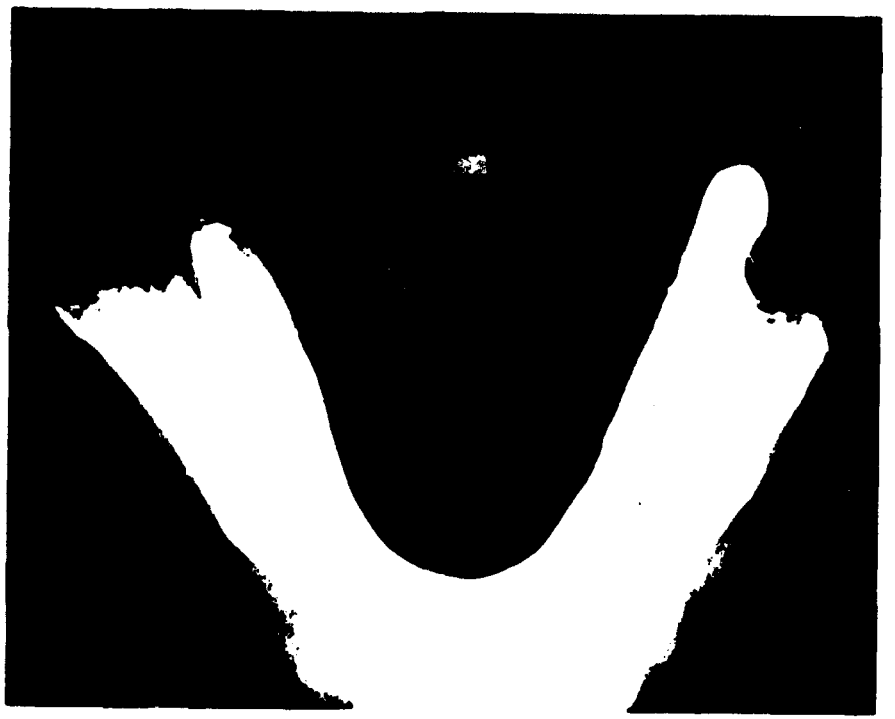
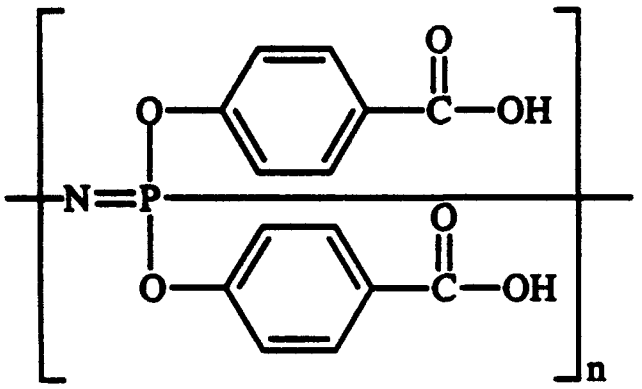


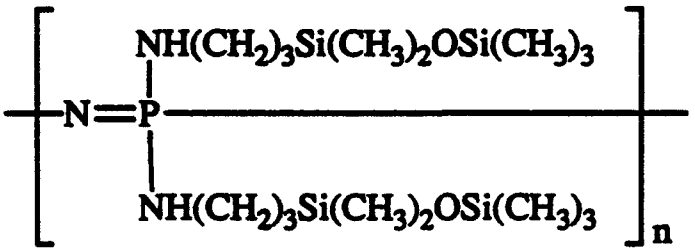
Figure 1. Poly(organophosphazene) shock absorbing denture liner. (Reprinted courtesy of Dr. L. Gettleman)(24)

Chart 1. Examples of Poly(organophosphazenes)



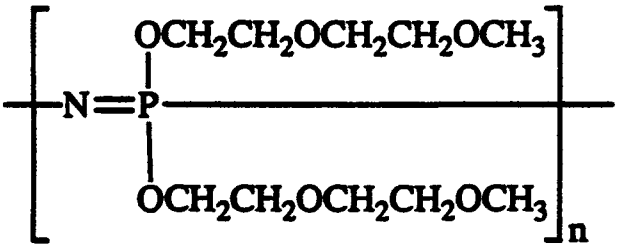
3

Water Soluble as Sodium Salt, Cross-linkable by Ca^{2+} Ions



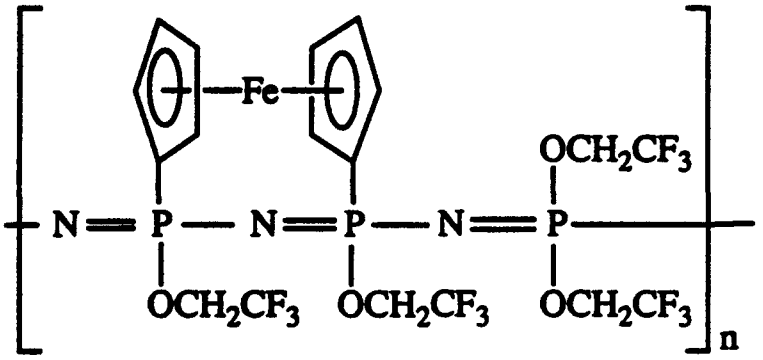
4

Elastomer



5

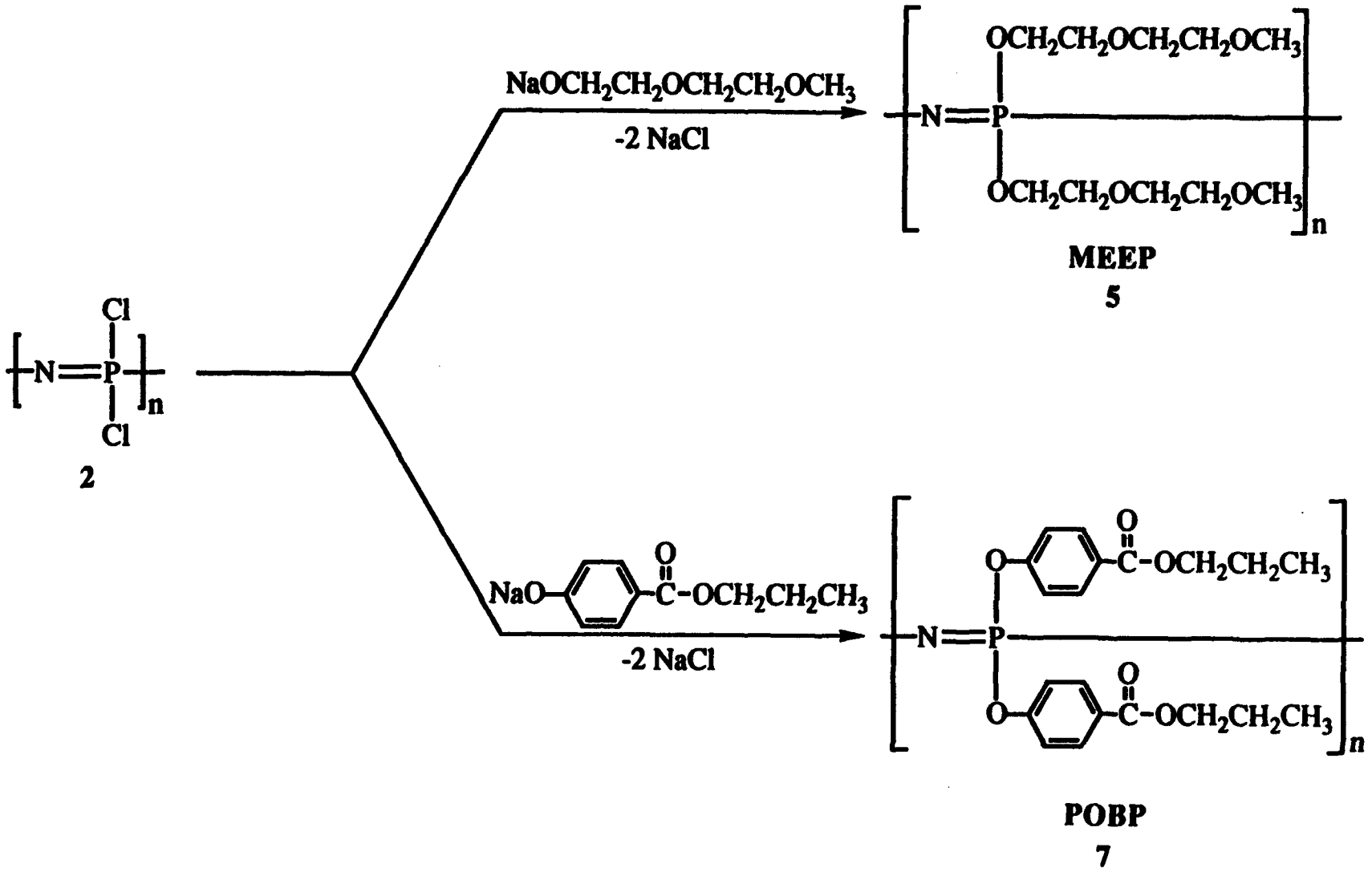
Water-Soluble, Solid Electrolyte



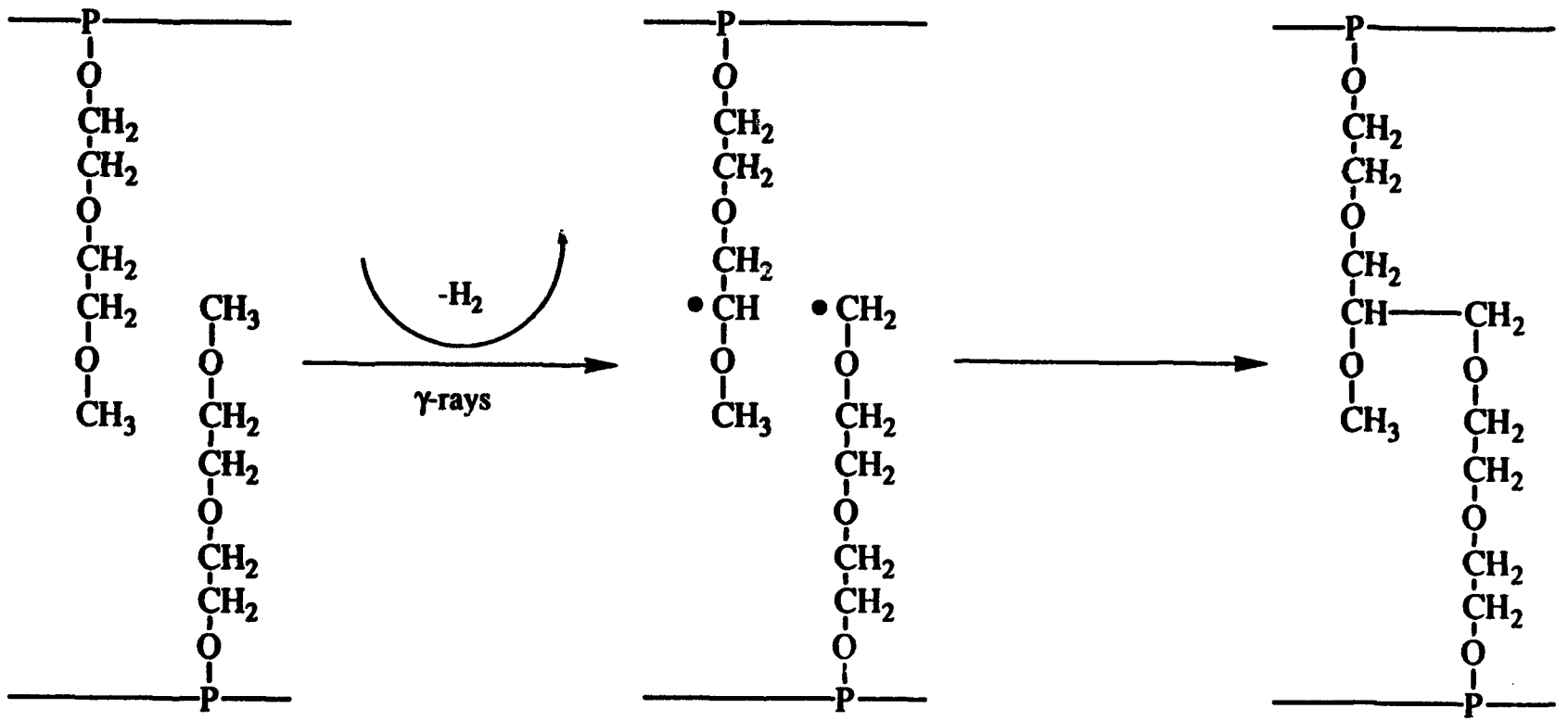
6

Electroactive Material

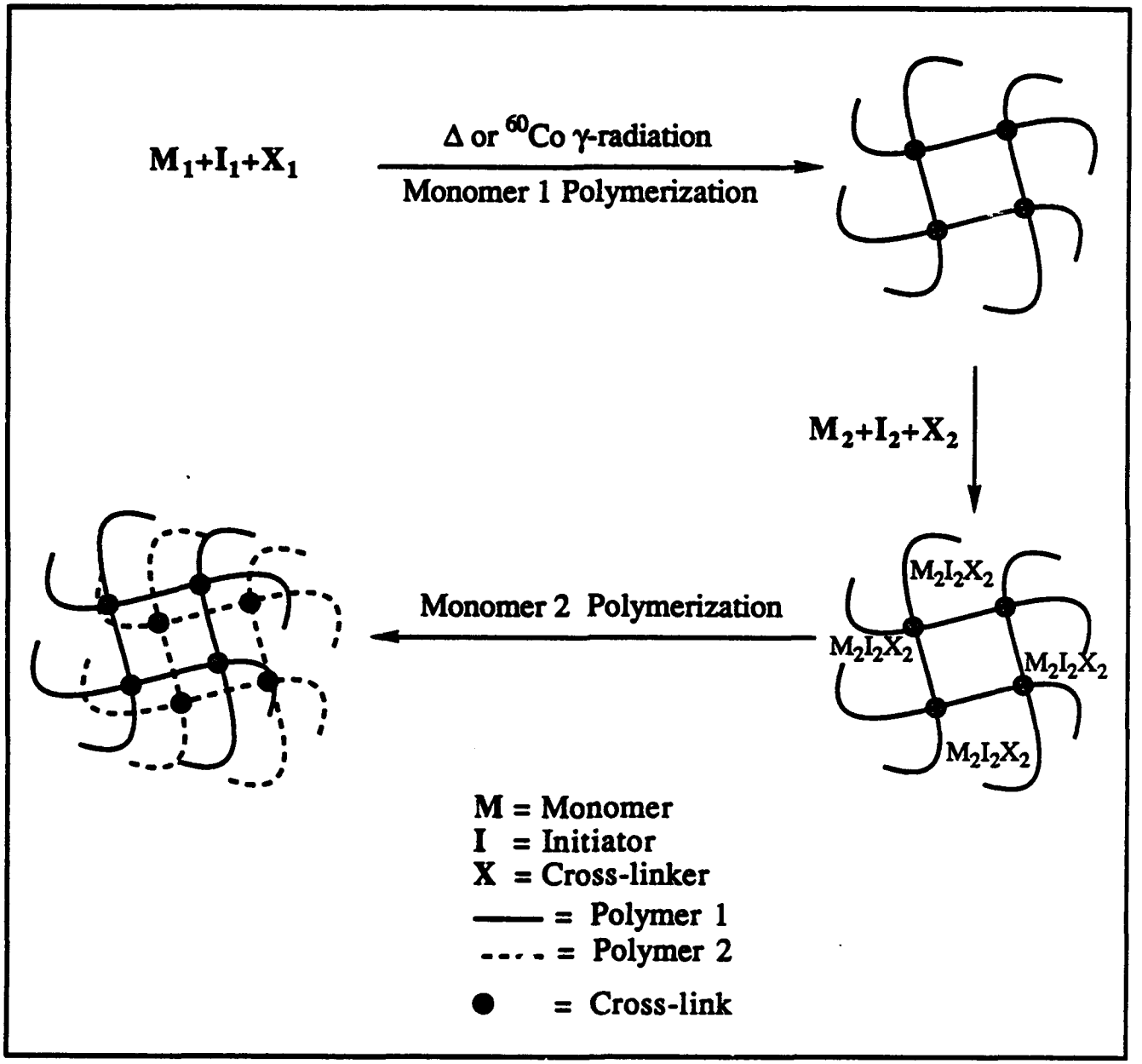
Scheme 3. Synthesis of Poly(organophosphazenes) Used in This Work



Scheme 4. Crosslinking of Poly(organophosphazenes) by ^{60}Co γ-Radiation [12]



Scheme 5. Schematic Representation of IPN Preparation



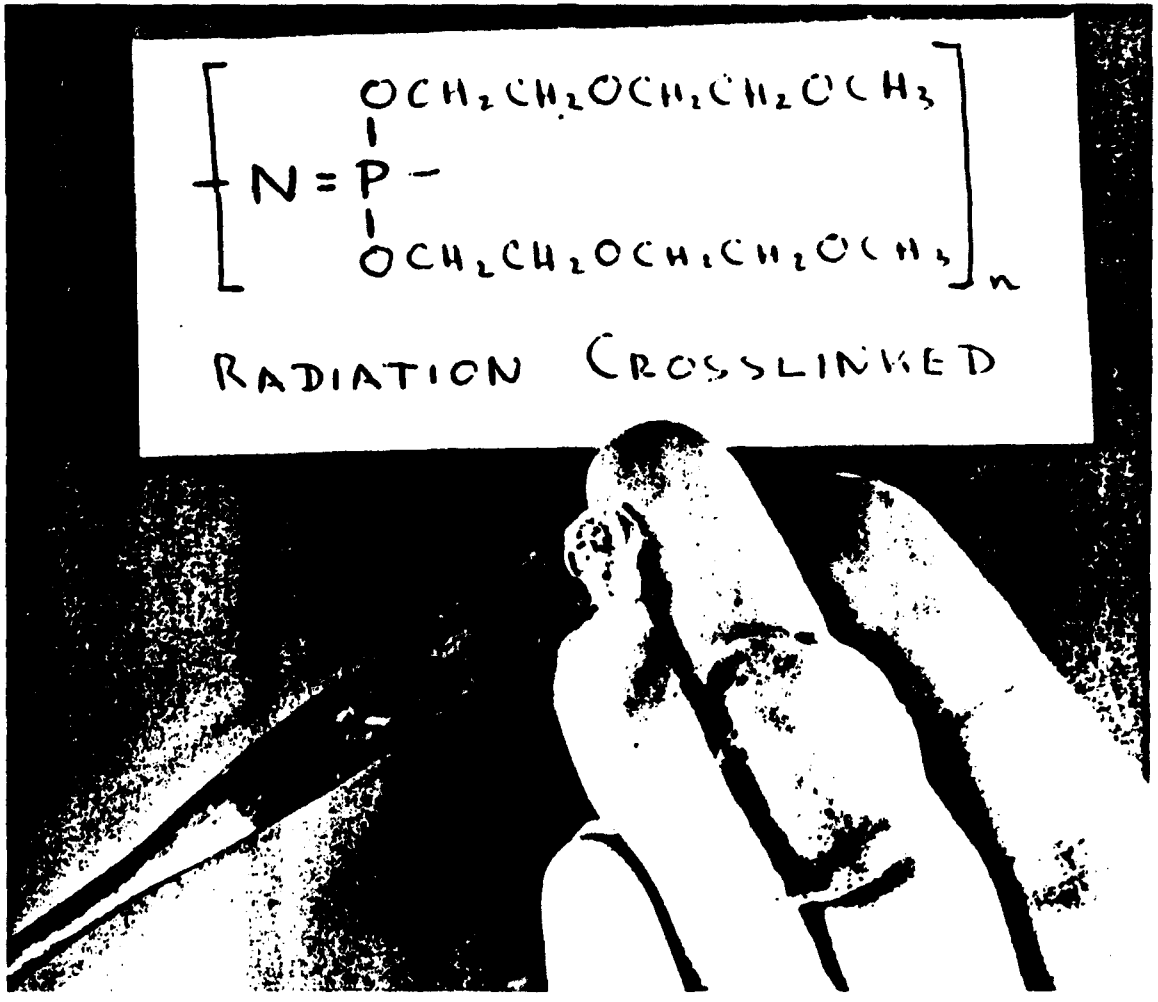
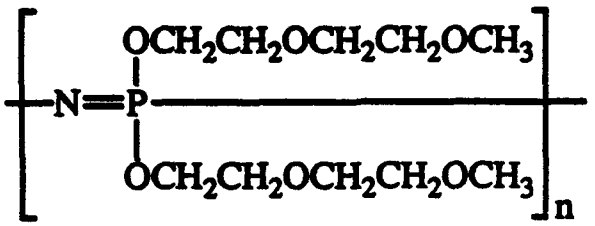


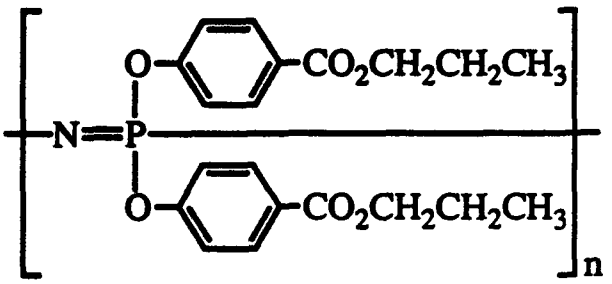
Figure 2. MEEP after cross-linking and after swelling in water for several hours. (Reprinted courtesy of Dr. H. R. Allcock)(12)

Chart 2. IPN Component Polymers

Poly(organophosphazenes)

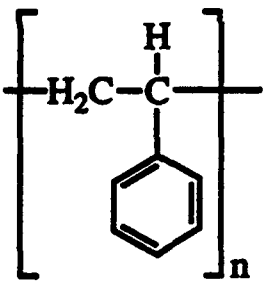


MEEP (5)

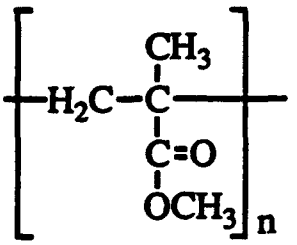


POBP (7)

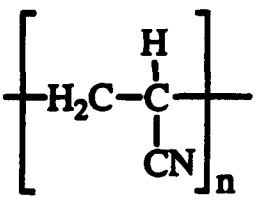
Organic Polymers



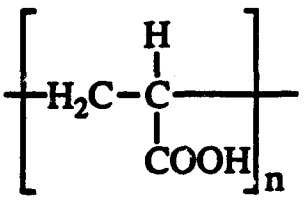
Polystyrene (PS) (8)



Poly(methyl methacrylate) (PMMA) (9)



Polyacrylonitrile (PAN) (10)



Poly(acrylic acid) (PAA) (11)

Scheme 6. Experimental Procedure for Preparation of Poly(organophosphazene) IPNs

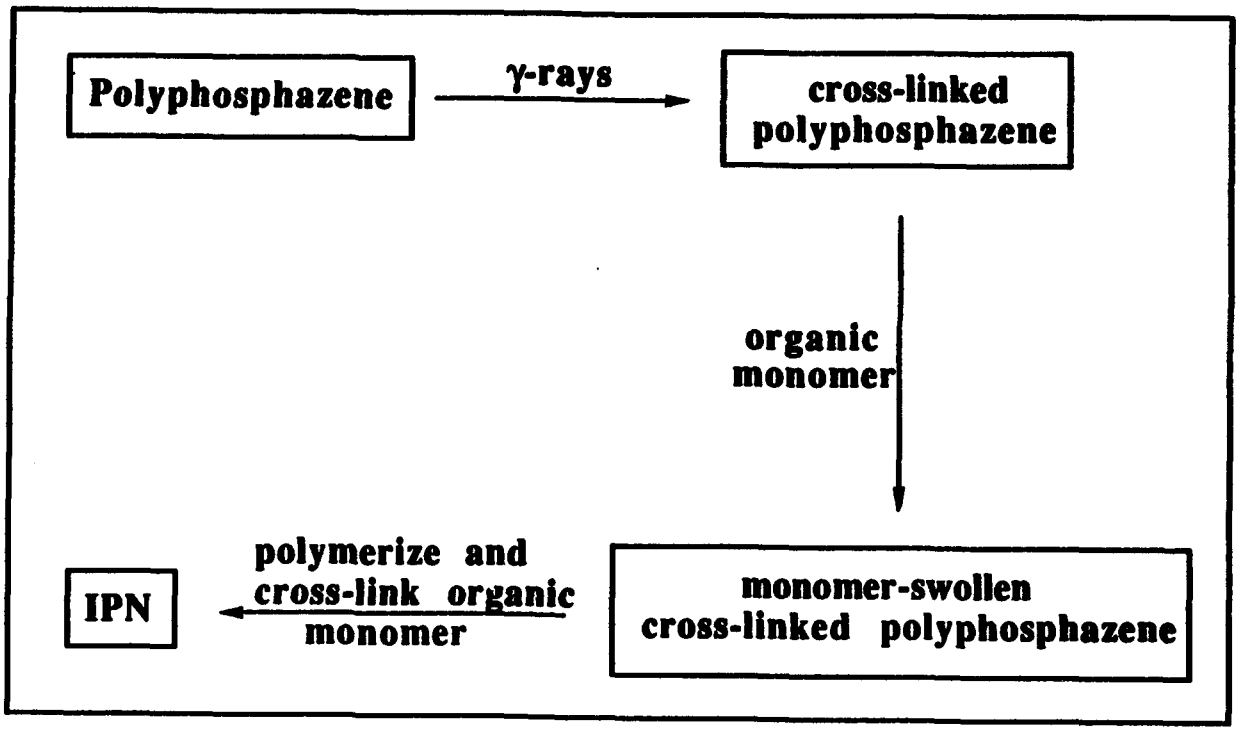


Table 2. IPN Component Ratios[a]

MEEP/PS (5/8)	1 : 1
MEEP/PMMA (5/9)	3 : 1
MEEP/PAN (5/10)	1 : 1
MEEP/PAA (5/11)	1 : 1
POBP/PS (7/8)	2.5 : 1
POBP/PMMA (7/9)	1.5 : 1
POBP/PAN (7/10)	4.5 : 1
POBP/PAA (7/11)	2 : 1

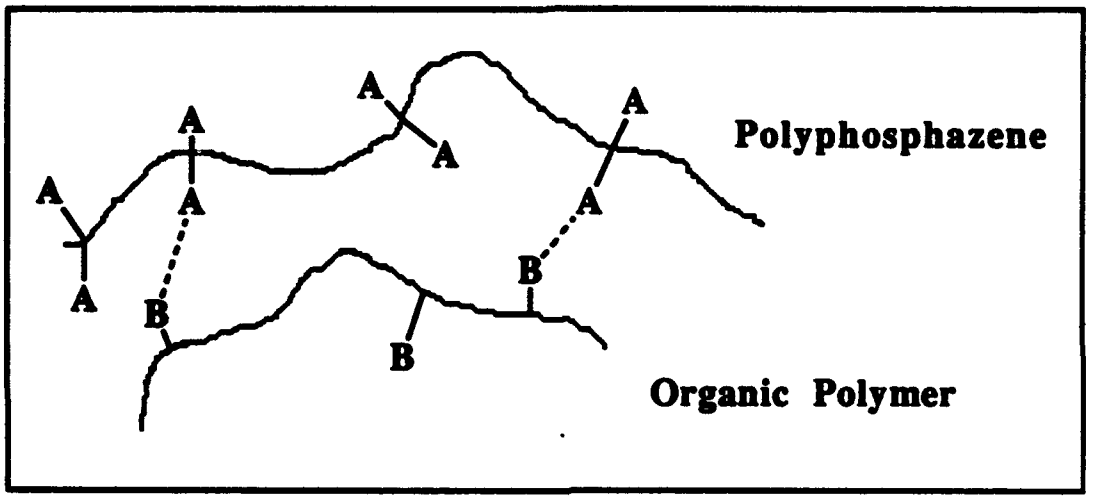
a: Based on NMR integration

Table 3. DSC Data and Tg's of Individual Component Polymers

IPN	Tg (°C)[a]
MEEP/PS (5/8)	-70/+57
MEEP/PMMA (5/9)	-80/+112
MEEP/PAN (5/10)	+34
MEEP/PAA (5/11)	-41/+3.5
POBP/PS (7/8)	-14/+92
POBP/PMMA (7/9)	-14/+50
POBP/PAN (7/10)	-9/+51
POBP/PAA (7/11)	+54

a: Component Polymer Tg's: MEEP(5)= -84 °C; POBP(7)= -23 °C;
PS(8) = 100 °C; PMMA(9) = 105 °C;
PAN(10) = 106 °C; PAA(11) = 85 °C

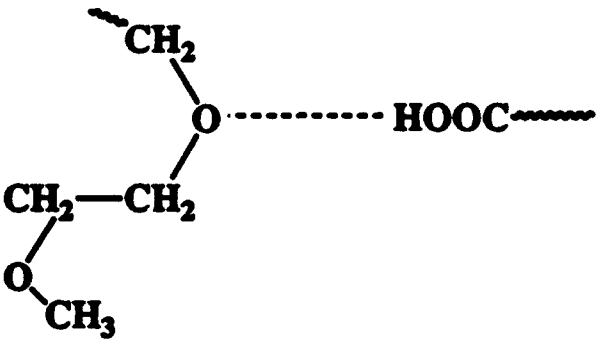
Scheme 7. Schematic Illustration of Intermolecular Interaction



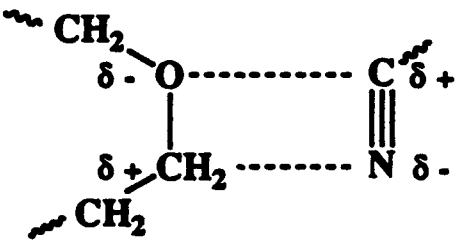
Scheme 8. Possible Molecular Level Interactions

Polyphosphazene	Organic Polymer

Hydrogen Bonding



Dipole-Dipole



van der Waals Interaction

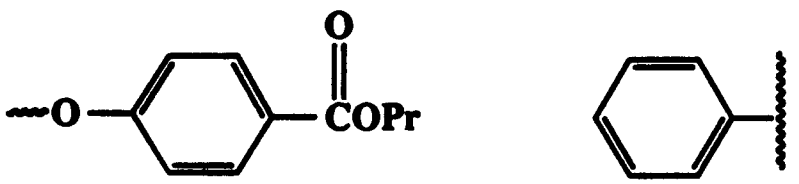


Figure 3. DSC Thermogram of MEEP(5)/PAN(10) IPN.

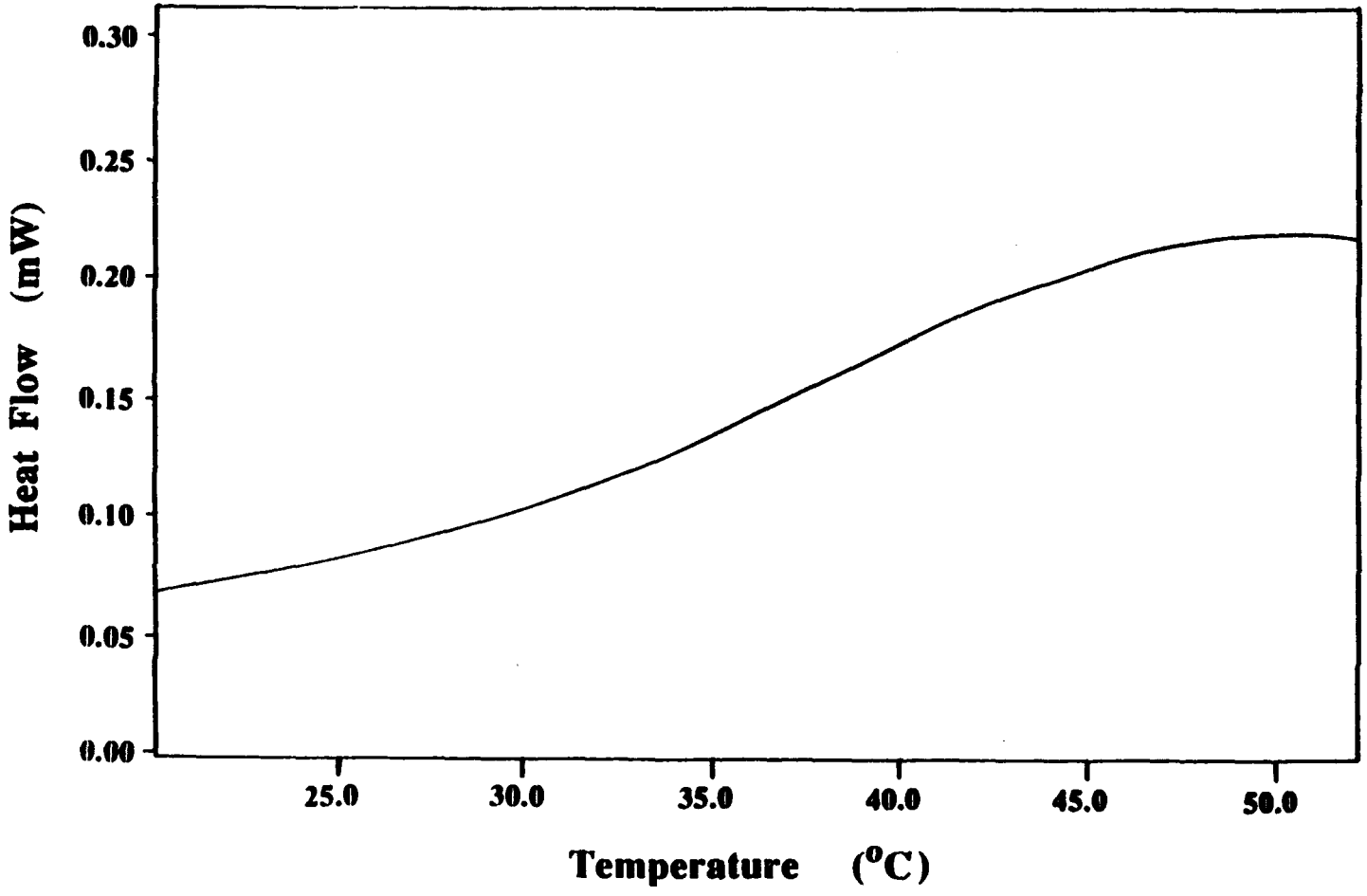
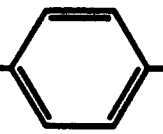
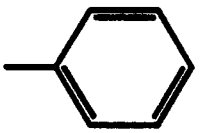


Table 4. Participating Side Groups and Possible Interactions

Polyphosphazene	
—$OCH_2CH_2OCH_2CH_2OCH_3$ (5)	H-Bond Acceptor Dipole-Dipole
—O—  —COOPr (7)	H-Bond Acceptor Hydrophobic
Organic Polymer	
 (8)	Hydrophobic
—COOMe (9)	H-Bond Acceptor Dipole-Dipole
—C≡N (10)	Dipole-Dipole
—COOH (11)	H-Bond Donor Dipole-Dipole

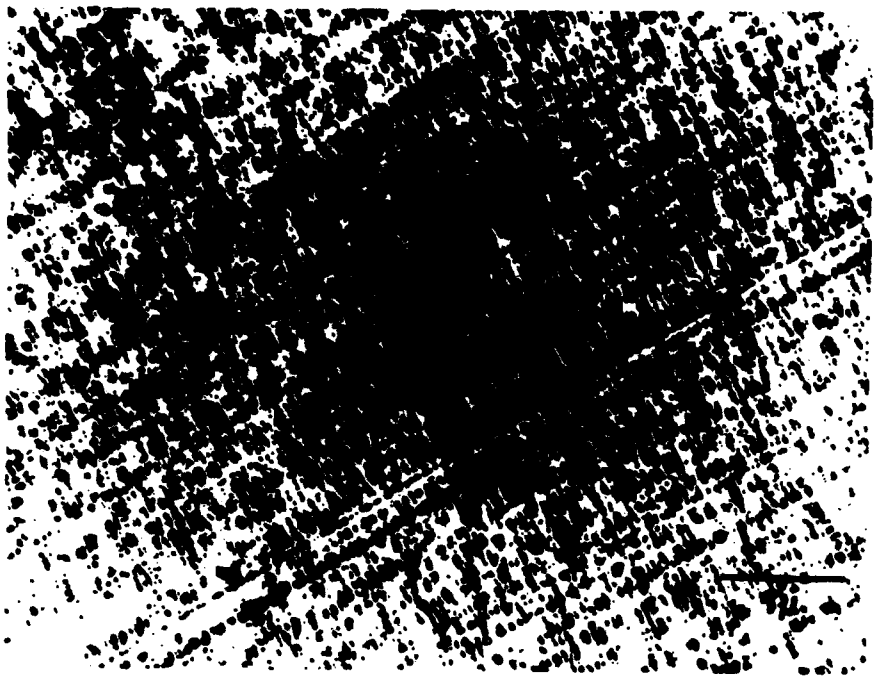


Figure 4. TEM Micrograph of MEEP(5)/PAN(10) IPN.

Figure 5. DSC Thermogram of POBP(7)/PS(8) IPN.

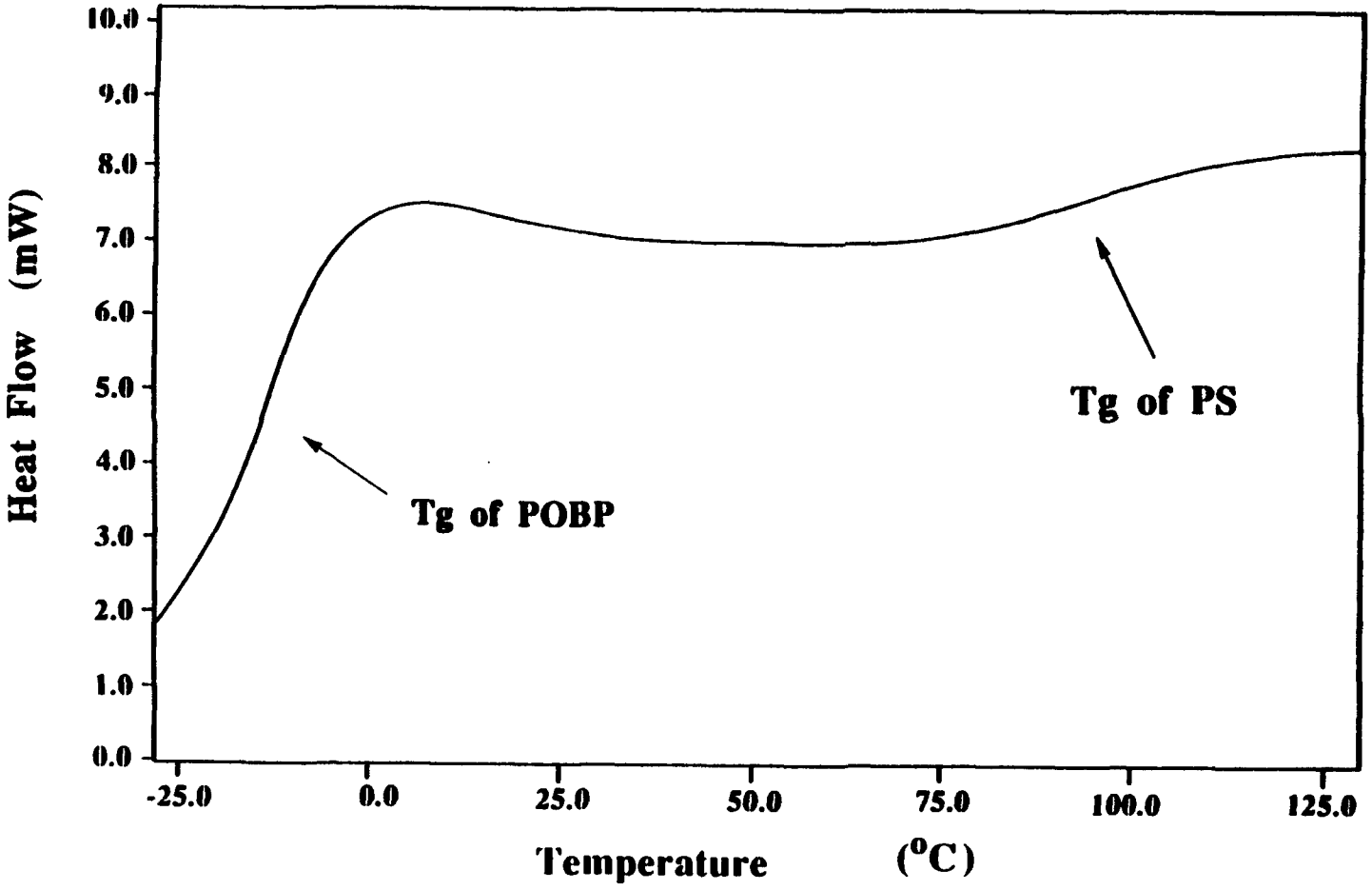


Figure 6. TEM Micrograph of POBP(7)/PS(8) IPN.

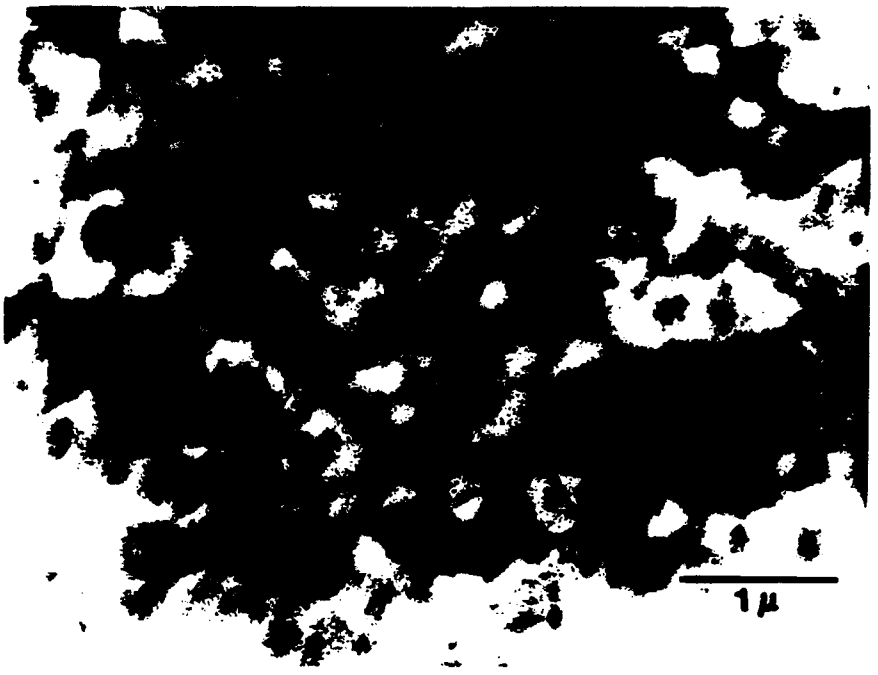


Figure 7. TEM Micrograph of MEEP(5)/PMMA(9) IPN.

Figure 8. TEM Micrograph of POBP(7)/PMMA(9) IPN.

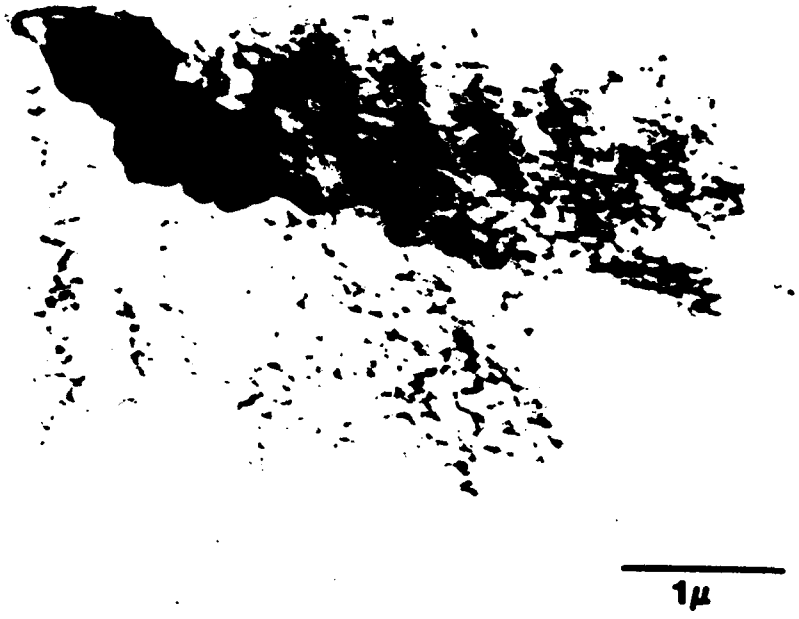


Figure 9. TEM Micrograph of POBP(7)/PAA(11) IPN.

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